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REACTIVITY COMPARISON
OF AN AUTOMOTIVE EXHAUST CATALYST
TO A PROPRIETARY CONTRACTOR SUPPLIED MATERIAL

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The reactivity of a commercially available automotive catalyst was compared to that of a contractor (Allied Signal) supplied material. Chloroacetonitrile was chosen to probe the washcoat activity of the two materials, while 2-chloroethyl ethyl sulfide was chosen to probe the external mass transfer properties of the two materials. Both the washcoat activity and external mass transport properties of the contractor supplied material were found to be superior to that of the automotive catalyst.

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PREFACE

The work described in this report was authorized under Contract No. DAAA15-91-C-0075, Improved Catalysts Materials and Modeling. This work was started in January 1992 and completed in May 1992.

Proprietary information is contained on page 7 of this report.

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Reactivity Comparison of an Automotive Exhaust Catalyst to a Proprietary Contractor Supplied Material

1. INTRODUCTION

Present air purification systems designed for removal of chemical warfare (CW) agents from air streams are based solely on activated, impregnated carbon, namely ASC whetlerite. Alternative air purification technologies are being investigated due to the loss of activity associated with the ASC whetlerite caused by reduction of the chromium(VI) impregnant[1]. The loss of activity imposes change-out requirements which may present logistical as well as disposal burdens. Several alternative filtration processes, such as pressure swing adsorption (PSA), temperature swing adsorption (TSA) and catalytic oxidation (Cat-Ox), are candidate technologies which may alleviate the above mentioned burdens.

Catalytic oxidation is a means of removing CW agents from streams of air. Lester and Marinangeli[2] have demonstrated that low concentrations (less than 1,000 ppm; 1,200 mg/m^3) of CW agents can be readily destroyed via catalytic oxidation. Klinghoffer and Rossin[3,4] have recently reported kinetic studies involving the oxidation of a cyanogen chloride model compound, namely chloroacetonitrile ($ClCH_2C \equiv N$), over a supported platinum catalyst. The results of their study indicated that acid gas reaction products may inhibit the reaction via adsorption onto catalytically active sites.

The objective of this study was to compare the performance of a contractor supplied catalytic material to that of a commercially available automotive emissions control catalyst. Probe molecules have been used to evaluate and compare the washcoat reactivity and external mass transfer properties of the two catalytic materials.

2. EXPERIMENTAL

2.1 Materials.

Reagent grade chloroacetonitrile (98+ %) and 2-chloroethyl ethyl sulfide (98 %) were purchased from Aldrich Chemical Company. Samples of the automotive monolith were obtained from a 1986 Honda Accord catalytic converter purchased from Kunkel's Auto Parts in Edgewood, Maryland. This material will be referred to as the Automotive catalyst through out the text. The Automotive catalyst core was obtained by drilling a section of the monolith block with a diamond core saw. A pre-cut sample of the contractor supplied monolith, termed Military Air Purification (MAP) catalyst, was received from Allied Signal.

2.2 Equipment.

A schematic representation of the fixed bed reactor system is illustrated in Figure 1. Dry, oil-free air from a PSA air drier was metered to the reactor using a 0-50 Nl/min mass flow controller. Nl (normal liter) is defined as one liter of dry air at 0°C and one atmosphere pressure. Dry air from the mass flow controller was then delivered to a water saturator. A back pressure regulator follows the water saturator. The concentration of water in the air stream was controlled by adjusting the temperature and pressure of the saturator. The saturator could be by-passed to conduct experiments in dry air.

Chloroacetonitrile and 2-chloroethyl ethyl sulfide were delivered to the reactor system as a saturated vapor from a sparger system. A separate stream of PSA dried air was metered to the sparger system using a 0-2 Nl/min mass flow controller. In the case of the chloroacetonitrile, the sparger system consisted of a series of three 250 ml polytetrafluoroethylene (PTFE) jars filled to approximately 75 % capacity with chloroacetonitrile. In the case of the 2-chloroethyl ethyl sulfide, the sparger consisted of one 250 ml PTFE jar filled to 50 % capacity with 2-chloroethyl ethyl sulfide. The air stream was bubbled through either liquid chloroacetonitrile or 2-chloroethyl ethyl sulfide contained within the sparger system. The sparger system was completely submerged in a temperature controlled, circulating water bath. A back pressure regulator was located down stream of the sparger system and was used to maintain a constant pressure over liquid contained within the sparger.

The concentrated feed stream from the sparger system was delivered to a static mixer which served to blend the reactant stream with the humid air stream. Following the static mixer, the feed stream was delivered to the catalytic reactor unit. The catalytic reactor consisted of a glass pre-heater and glass reactor. The pre-heater consisted of a 2.54 cm o.d. by 66 cm long glass tube filled with 4 mm glass beads. The glass beads provided further mixing of the feed gas as well as surface area for improving the heat transfer properties of the unit. The pre-heater was housed in an 8.9 cm diameter aluminum block. The aluminum block was heated using two independent 8 m bead heaters. The temperature of the pre-heater was controlled by controlling the temperature of the aluminum block.

The reactor consisted of a 3.8 cm o.d. by 50 cm long glass tube for the Automotive catalyst. For the MAP catalyst, the reactor consisted of a 4.1 cm o.d. by 50 cm long glass tube. A different reactor was required to house the MAP catalyst, as its diameter was slightly greater than the reactor used with the Automotive catalyst. The reactor was connected to the pre-heater via a 10 cm diameter glass flange. The joint connecting the two segments could not be heated due to the temperature limit associated with the gasket. However, the joint was insulated to minimize any heat loss. The first 14 cm of the of the reactor was packed with 4 mm glass beads to provide additional heating of the feed stream. The catalyst core was located approximately 7 cm below the glass bead zone within the reactor. The Automotive catalyst core employed in this study was
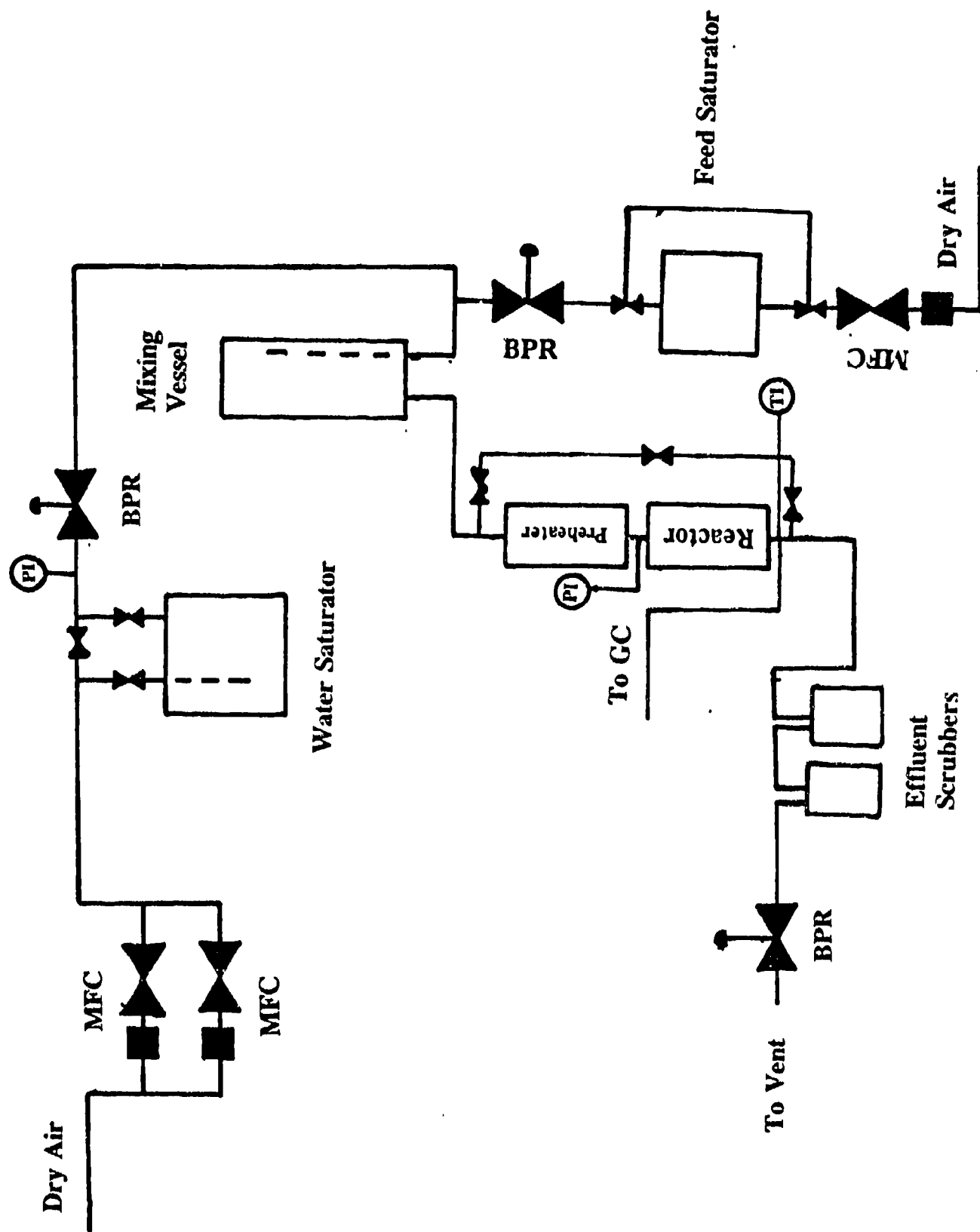
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Figure 1: Schematic Representation of the Fixed-Bed Reactor System.

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5.4 cm in length. Five fine wire thermocouples were located at discrete axial positions within the channels of the monolith. Each thermocouple was located in a separate, unobstructed channel. The MAP catalyst core was 10.5 cm in length. Different linear velocities are required for each catalyst in order to achieve a similar residence time. However, theory predicts that linear velocity will not have an effect on the external mass transfer properties of either catalyst, due to the flow being laminar within the monolith channels. Three fine wire thermocouples were located at discrete axial positions within the channels of the MAP catalyst, with each thermocouple located within a separate, unobstructed channel. The reactor unit was housed in an 8.9 cm diameter aluminum block. The reactor block was heated using an 8 m bead heater. The temperature of the catalyst was controlled by controlling the temperature of the aluminum block and the incoming feed stream.

Reactor effluent was delivered to two scrubber tanks filled with water. The scrubber tanks arc located just after the point where the effluent gas is sampled. The purpose of the tanks was to remove acid gas reaction products from the effluent stream, preventing these gases from damaging the back pressure regulator, which was located just after the scrubber tanks and was used to maintain a constant pressure of 4.5 psig on the reactor. Following the back pressure regulator, the effluent was vented to a fume hood.

2.3 Sample Analysis.

Chloroacetonitrile feed and effluent streams were analyzed using an HP 5890 gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). 2-chloroethyl ethyl sulfide feed and effluent streams were analyzed using an HP 5890 gas chromatograph equipped with an FID and flame photometric detector (FPD). The FID was used to quantitatively analyze the feed and effluent streams for chloroacetonitrile. The TCD was used to analyze the reactor effluent for CO_2 during the chloroacetonitrile experiments. The FPD was used to analyze the feed and effluent streams for 2-chloroethyl ethyl sulfide. An electrically actuated ball valve was located up stream of the GC sample valve. The ball valve was closed for 30 seconds prior to sample injection in order to depressurize the sample loop. Chloroacetonitrile and 2-chloroethyl ethyl sulfide were analyzed on a 10 % OV-210 on 60/80 mesh Supelcoport glass GC column. CO_2 was analyzed on a 2 m Hayescp Q stainless steel column.

2.4 Catalyst Preparation.

The Automotive and MAP monolith cores were prepared following a similar procedure. The center of the catalyst cores were plugged with alundum cement so as to leave a ring of one to two channels around the monolith circumference unobstructed. The bottom of each core was also plugged in this manner to prevent any reactivity due to back mixing of the feed stream. The outer diameter of the core was coated with a thin layer of alundum cement, then wrapped with a thin layer of glass wool in order to provide a seal

with the reactor wall, thus preventing by-passing of the catalyst. Fine wire thermocouples were then placed at discrete locations within open channels of the monoliths to measure the axial temperature gradients. Once complete, the reactor was returned to the system.

Both catalysts were heated in dry air *in-situ* to 400°C at a rate of 40°C per hour. This temperature was maintained overnight, after which, the run was initiated, as described below.

2.5 Reactivity Measurements.

Four experiments with each catalyst (Automotive and MAP) were conducted with chloroacetonitrile to measure and compare the reactivity of each catalyst. Reactivity is defined as the ability of the catalyst to decompose the reactant molecule. Two concentrations, 1000 and 3500 ppm, and two residence times (τ), 0.05 and 0.10 seconds, were employed in this study. All experiments were conducted in humid air with a reactor pressure of 4.5 psig. The run was initiated by introducing chloroacetonitrile to the feed stream. The initial catalyst temperature was maintained at 400°C for two hours. After this time, the catalyst temperature was decreased to 250°C at a rate of 30°C per hour. Effluent analysis was performed every 30 minutes (15°C) and conversions were recorded as a function of temperature. The recorded temperature was the average of the temperature measurements within the channels of the monolith. Typically, this temperature did not deviate by more than 3°C over the length of the monolith. At the end of each run, the catalyst temperature was raised to 400°C overnight in flowing humid air. ·

Four experiments with 2-chloroethyl ethyl sulfide were conducted to compare the mass transfer properties of the Automotive and MAP catalysts. One concentration, approximately 50 ppm (265 mg/m^3), and two residence times (τ), 0.03 and 0.05 seconds, were employed in this study. All experiments were conducted in dry air because water was shown to have virtually no effect on the catalytic activity of the Automotive catalyst. For the Automotive catalyst, the effluent concentration of 2-chloroethyl ethyl sulfide was recorded for each residence time at temperatures of 300, 325, 350, 375, 400, 420 and 440°C. The process conditions were maintained for approximately 2 hours. For the MAP catalyst, an initial temperature of 350°C was maintained for two hours following the introduction of 2-chloroethyl ethyl sulfide to the feed stream. The catalyst temperature was then decreased to 150°C at a rate of 20°C per hour. Effluent analysis was performed every 15 minutes (5°C). The recorded temperature was the average of the temperatures measured within the monolith core. At the end of each run, the catalyst was heated to the initial temperature overnight in flowing dry air.

A final, experiment was conducted with chloroacetonitrile to identify the reaction products. The experiment was run in the absence of nitrogen in the feed stream for the purpose of determining whether nitrogen (N_2) was formed as a reaction product. Ultra high purity helium and O_2 were delivered to the system in the place of the PSA dried air. A blank run was done to verify the absence of N_2 in the system. The effluent was

analyzed using an HP 5890 gas chromatograph equipped with a TCD. The sample separation was performed using a 3.6 m 100/120 Carbosieve SII packed stainless steel column. The experiment was conducted with a reactor temperature of 400°C and a chloroacetonitrile feed concentration of 2,000 ppm with a residence time of 0.1 seconds. Under these conditions, the conversion of chloroacetonitrile was complete. The reactor effluent stream was analyzed for the presence of nitrogen containing products.

3.   RESULTS AND DISCUSSION

The two compounds selected for testing, chloroacetonitrile and 2-chloroethyl ethyl sulfide, were chosen to probe specific properties of the two catalytic materials. Chloroacetonitrile, a model compound for cyanogen chloride, was selected for the purpose of comparing the washcoat properties of the two catalysts. Previous experience with chloroacetonitrile suggested that for the range of conditions being evaluated in this study, the oxidation reaction will not be significantly influenced by external mass transfer. 2-chloroethyl ethyl sulfide, a model compound for mustard, was chosen for the purpose of comparing the external mass transfer properties of the two catalysts. Previous experience with 2-chloroethyl ethyl sulfide has indicated that for the low concentrations being evaluated in this study (50 ppm, 265 mg/m^3), the reaction will be strongly influenced by external mass transfer.

3.1   Oxidation of Chloroacetonitrile.

Figures 2 and 3 compare conversion as a function of temperature for the oxidation of 1,000 ppm (3,369 mg/m^3) of chloroacetonitrile in humid air at residence times of 0.05 and 0.10 seconds, respectively, for the MAP and Automotive catalysts. Figures 4 and 5 compare conversion as a function of temperature for the oxidation of 3,500 ppm (11,790 mg/m^3) of chloroacetonitrile in humid air at residence times of 0.05 and 0.10 seconds, respectively, for the MAP and Automotive catalysts. As the results presented in Figures 2 - 5 show, the MAP catalyst is significantly more reactive than the Automotive catalyst. For example, for a challenge concentration of 3,500 ppm at 350°C and a residence time of 0.05 seconds (Figure 4), the MAP catalyst achieves a conversion of 92%, while the Automotive catalyst achieves a conversion of 35 %. At lower reaction temperatures, the deviation in conversions obtained with the two catalyst was less. For example, for a challenge concentration of 1,000 ppm at about 275°C and a residence time of 0.05 seconds (Figure 2), the MAP catalyst achieves a conversion of 43%, while the Automotive catalyst achieves a conversion of 30%. The slopes of the conversion versus temperature curves are steeper for the MAP catalyst, especially for data recorded with a challenge concentration of 1,000 ppm. The steeper slopes obtained with the MAP catalyst suggest a greater apparent activation energy.

Table 1 reports the apparent activation energy calculated at each of the 4 conditions for the two catalysts. These values were calculated from conversions recorded

Figure 2: Conversion as a Function of Temperature for the Oxidation of Chloroacetonitrile Over the Automotive and MAP Catalysts. [C] = 1,000 ppm, τ = 0.05 s

Figure 3:   Conversion as a Function of Temperature for the Oxidation of Chloroacetonitrile Over the Automotive and MAP Catalysts. [C] = 1,000 ppm, $\tau = 0.10$ s

Figure 4: Conversion as a Function of Temperature for the Oxidation of Chloroacetonitrile Over the Automotive and MAP Catalysts. [C] = 3,500 ppm, τ = 0.05 s
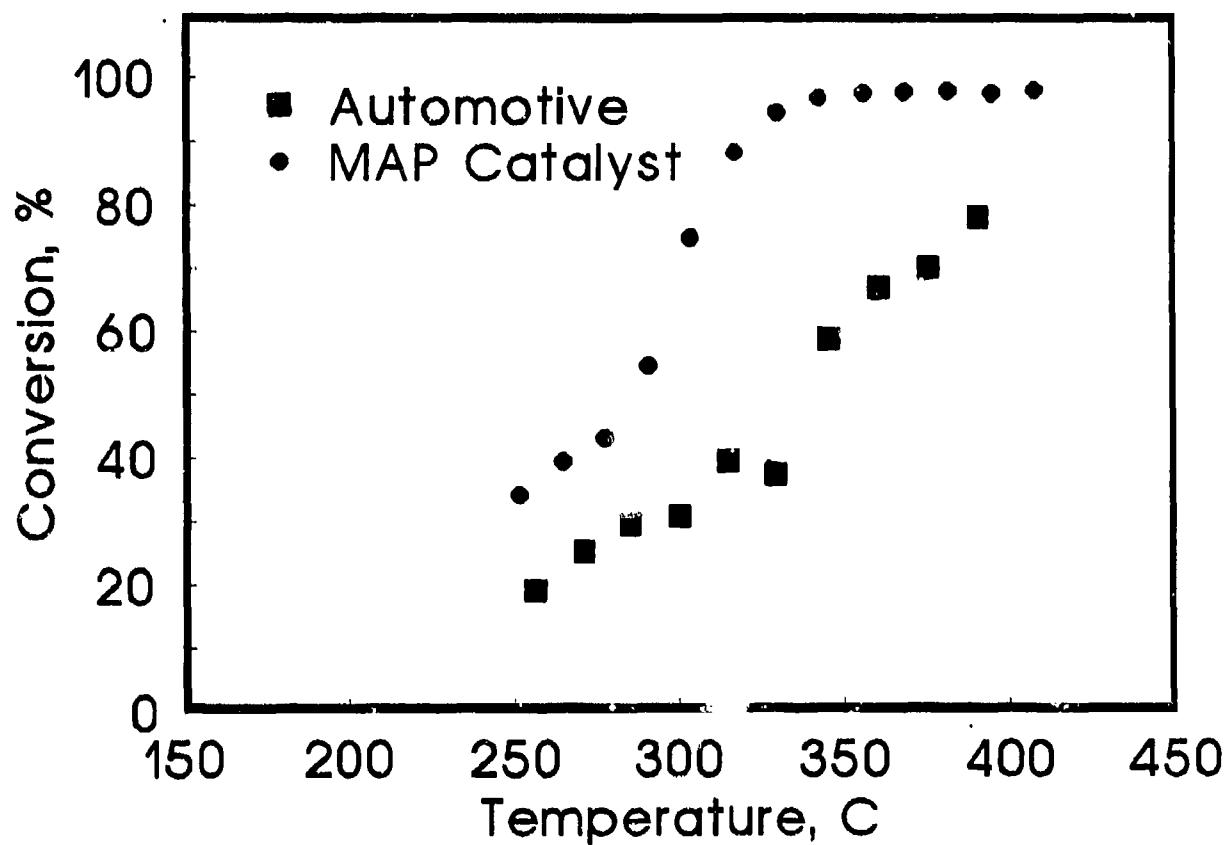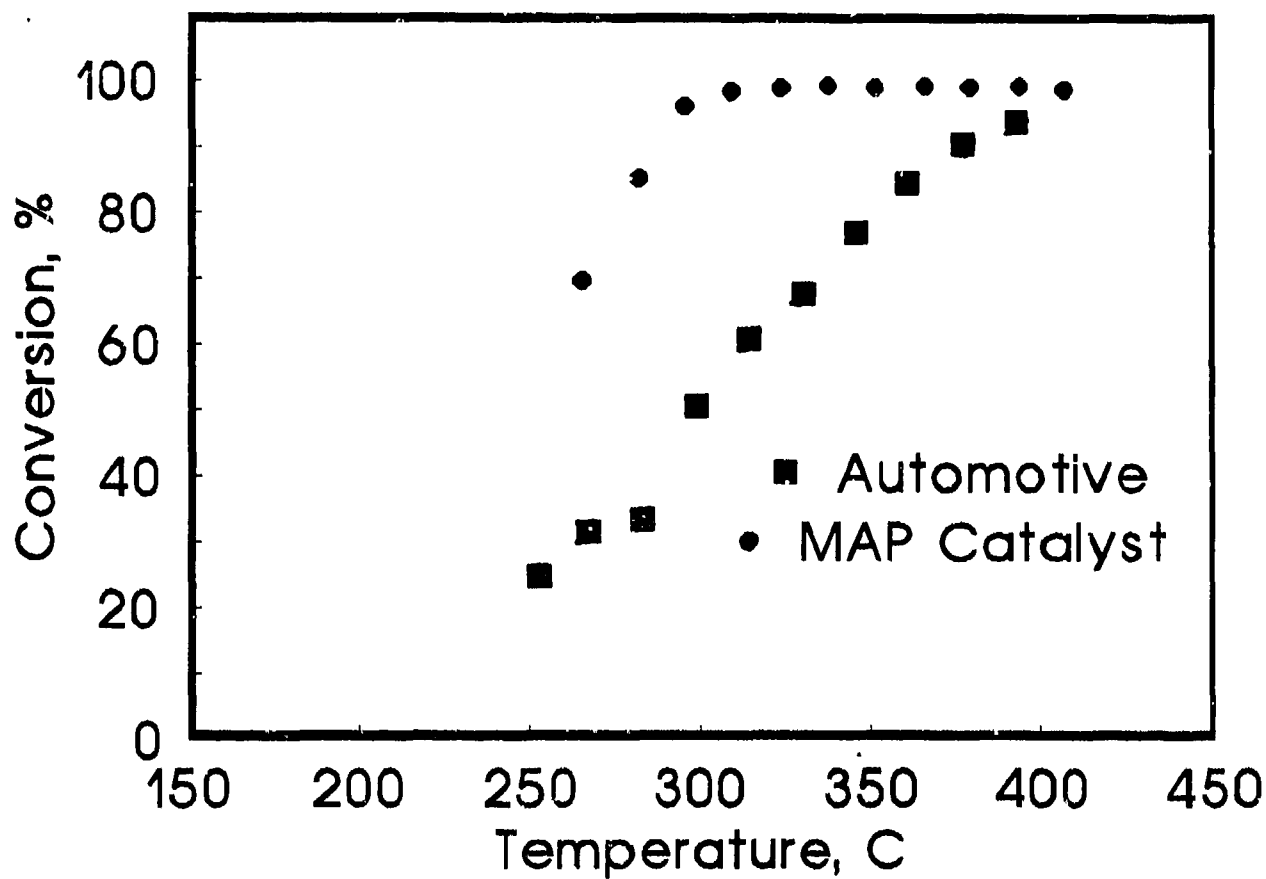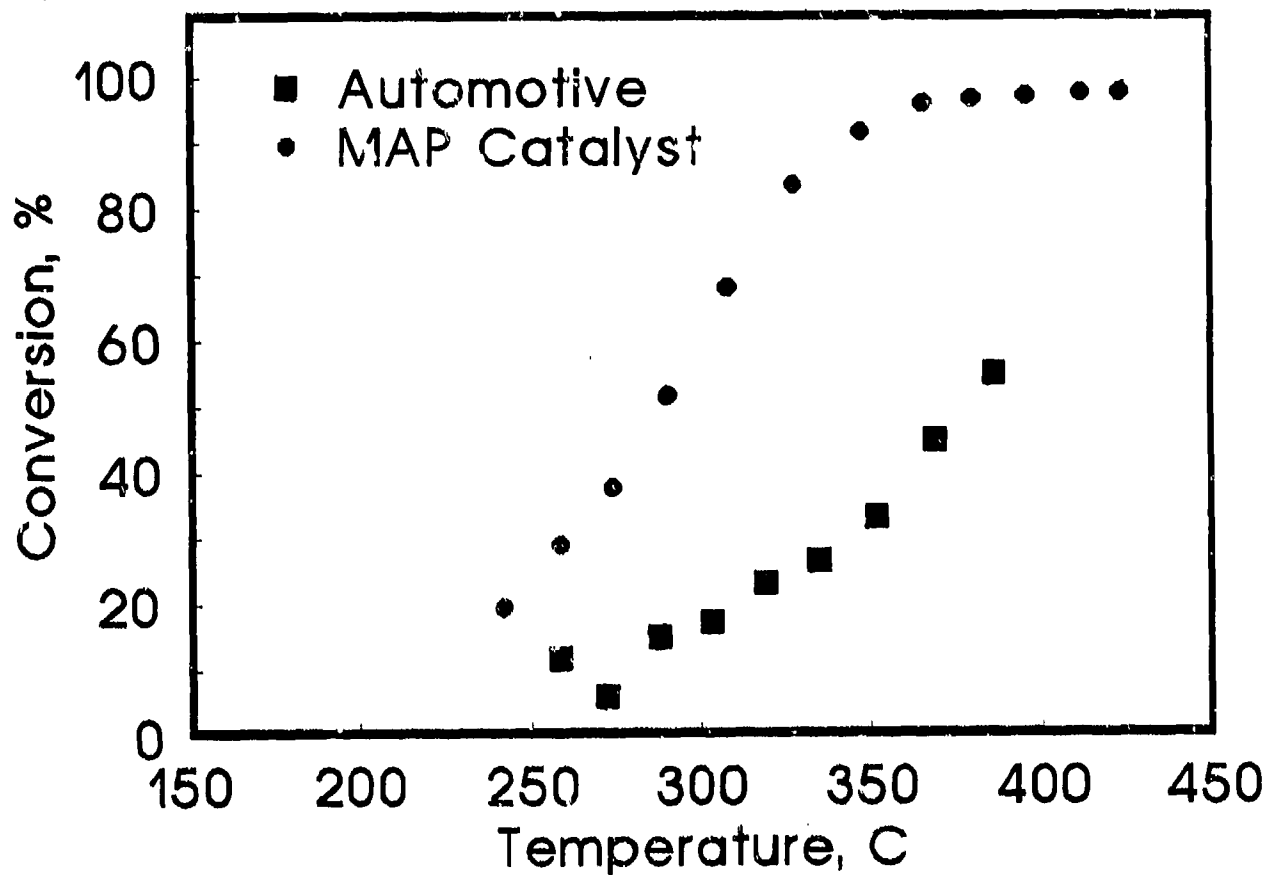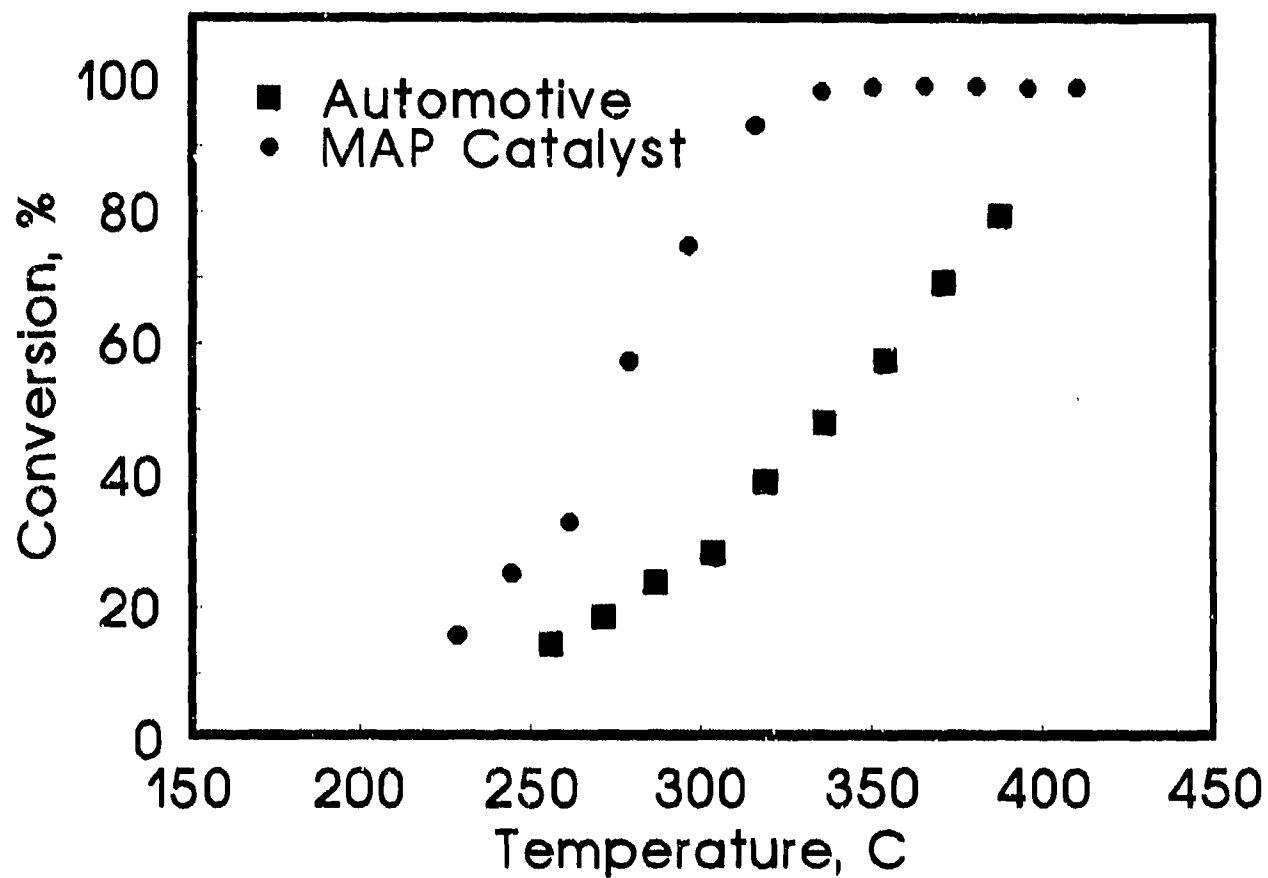
Figure 5:   Conversion as a Function of Temperature for the Oxidation of Chloroacetonitrile Over the Automotive and MAP Catalysts. [C] = 3,500 ppm, τ = 0.10 s

at temperatures below about 330°C for the MAP catalyst. At reaction temperatures greater than about 350°C, the apparent activation energy corresponding to the MAP catalyst was calculated to be approximately 1,000 to 1,500 cals/mol, indicating that the reaction was being limited by external mass transfer resistances. For the Automotive catalyst, the apparent activation energies are reported over the entire range of conditions. The apparent activation is defined as the activation energy calculated from the conversion versus temperature curve assuming the reaction proceeds via a first order process. The results presented in Table 1 show that the apparent activation energy is greater for the MAP catalyst. For the data recorded at 1,000 ppm, the apparent activation energy calculated for the MAP catalyst are approximately twice that obtained for the Automotive catalyst; 23,700 cal/mol versus 12,000 cal/mol. This result suggests that for this concentration, intraparticle mass transfer resistances are significant for the Automotive catalyst, but not very significant for the MAP catalyst[5]. Increasing the challenge concentration to 3,500 ppm results in a slight increase in the apparent activation energy calculated for the Automotive catalyst, suggesting that the mass transfer resistances are less significant for the higher concentration. For the MAP catalyst, the increase in the challenge concentration results in decreasing the apparent activation energy. One possible reason for this decrease is that the reaction is inhibited by the formation of reaction product, as has been previously reported[4]. By this, the decrease in the adsorption equilibrium constant with increasing temperature would be off-set by the increase in the reaction product concentration resulting from the higher conversion. The activation energy corresponding to the MAP catalyst is slightly greater (about 2,500 cal/mol) than that corresponding to the automotive catalyst.

Table 1
Apparent Activation Energies for the Oxidation of Chloroacetonitrile

Catalyst	Residence Time, s	Concentration, ppm	E_a, cal/mol-K
Automotive	0.05	1,100	11,400
Automotive	0.10	1,100	12,700
Automotive	0.05	3,750	17,000
Automotive	0.10	3,550	14,600
MAP	0.05	1,000	22,400
MAP	0.10	1,050	25,000
MAP	0.05	3,500	15,700
MAP	0.10	3,300	19,700

Figure 6 shows an Arrhenius plot of the global first order rate constant as calculated for the Automotive and MAP catalyst. These data were recorded for the 1,000 ppm challenge at a residence time of 0.05 seconds. Results show that at approximately 340°C, the activation energy decreases from 22 to 1 kcal/mol for the MAP catalyst, while the change in activation energy is not observed for the Automotive catalyst. The sharp decrease in the activation energy for the MAP catalyst observed at about 340°C is
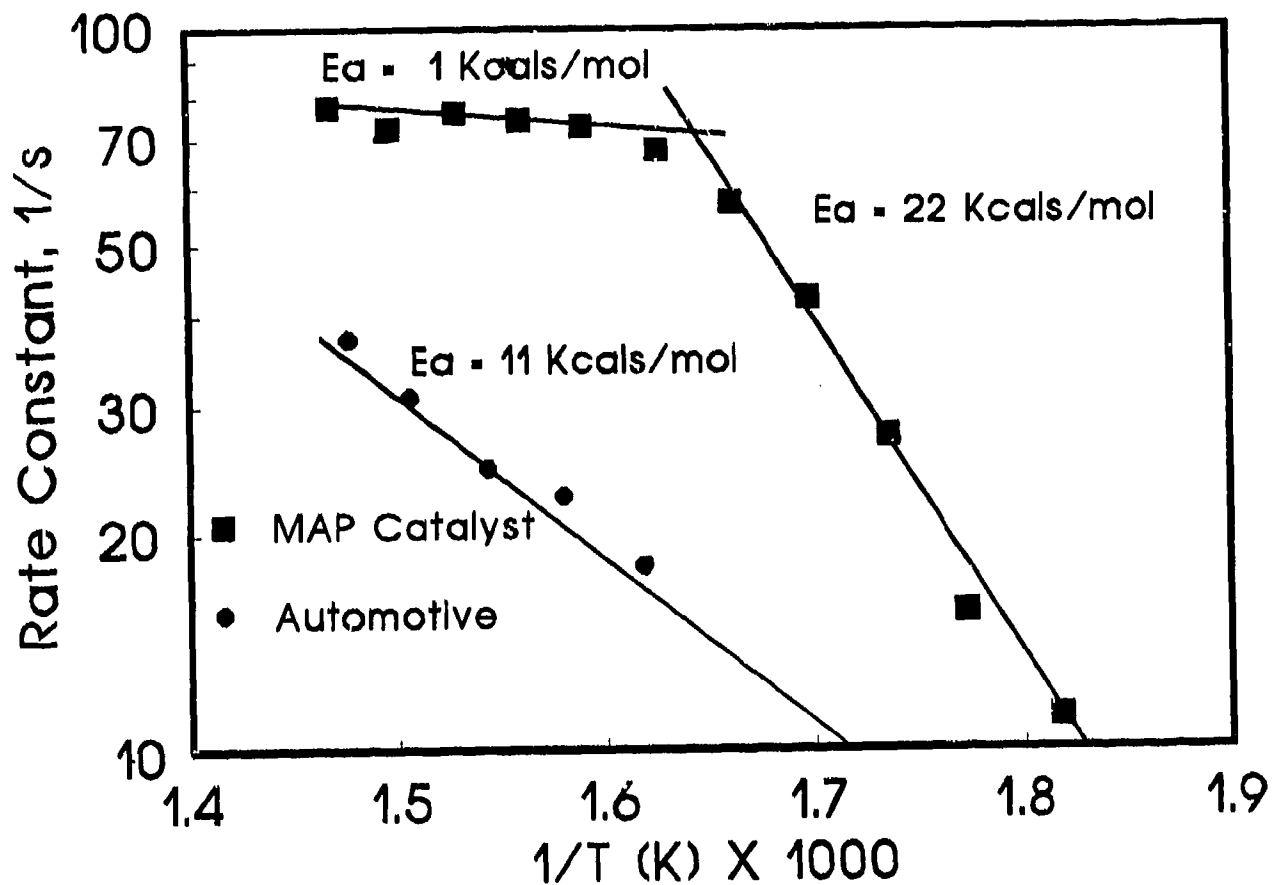
Figure 6: Arrhenius Plot of the Apparent First Order Rate Constant for the Automotive and MAP Catalysts. Oxidation of chloroacetonitrile, [C] = 1,000 ppm, τ = 0.05 s.

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attributed to the reaction shifting from a kinetically controlled regime to a mass transfer controlled regime. For the Automotive catalyst, the activity was significantly less than that of the MAP catalyst, and, as a result, external mass transfer never became the limiting step in the reaction scheme.

By comparing the data presented in Figures 3 and 5, the effect of concentration on conversion can be evaluated. Using the data from the MAP catalyst as an example, at 280°C and a residence time of 0.10 seconds, conversion increases from 58 to 85 % when the concentration is decreased from 3,500 to 1,000 ppm. This result demonstrates that the reaction is not first order in the concentration of chloroacetonitrile.
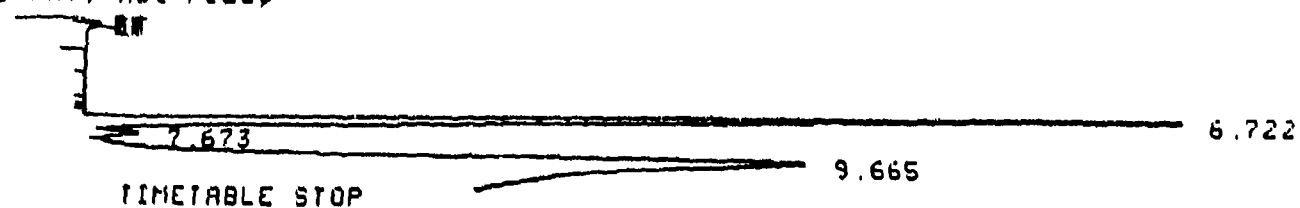
A test was conducted in the presence of helium and oxygen to assess the reaction products formed during the oxidation of chloroacetonitrile. The objective of this test was to determine if the nitrogen atom in chloroacetonitrile was being converted to nitrogen gas (N_2). The feed stream was 2,000 ppm (6,737 mg/m^3) chloroacetonitrile, 16.7 % oxygen, 3.5 % water, and the balance helium. All traces of nitrogen were removed from the system prior the beginning the experiment. A sample GC trace is illustrated in Figure 7. The concentration of nitrogen in the reactor effluent was approximated to be 1,000 ppm, indicating that the vast majority of the nitrogen associated with the chloroacetonitrile was converted to nitrogen gas, rather than oxides of nitrogen. This test was conducted at only one set of process conditions, therefore, the effects of concentration, temperature, pressure and conversion on the yield of nitrogen gas is not known at this time.

3.2   Oxidation of 2-Chloroethyl Ethyl Sulfide.

Figures 8 and 9 report the effluent concentration as a function of reaction temperature for the oxidation of 2-chloroethyl ethyl sulfide in dry air at residence times of 0.03 and 0.05 seconds, respectively. Data presented in these figures are reported for the MAP and Automotive catalysts. Effluent concentrations (below about 1 ppm), rather than conversions, are reported for two reasons. First, 2-chloroethyl ethyl sulfide is used as a model compound for mustard, where a maximum field concentration of approximately 32 ppm (225 mg/m^3) may be expected. The maximum allowable effluent concentration for mustard is 2.4 ppb (.0167 mg/m^3), based on U.S. Air Force requirements. Thus, a conversion of 99.9926 % is required. It was felt that testing the catalyst at conversions less than 95 % would provide information that is not consistent with the application. At high conversions, external mass transfer resistances become significant, and it was the intent of this portion of the study to probe the external mass transfer properties of the two catalysts. The second reason for reporting the low effluent concentrations has to do with the catalyst's activity. Both catalysts are highly reactive towards 2-chloroethyl ethyl sulfide. Operating at conditions such that conversions between 20 and 90 % would be maintained would not be consistent with the application.

Data reported in Figures 8 and 9 corresponding to the Automotive catalyst follow the expected trends, i.e., the effluent concentration decreases slowly with increasing

```
*  RUN #  723     APR  8, 1992  15:46:16
START: not ready

               7.673                                                            6.722

        TIMETABLE STOP                              9.665


RUN#    723            APR  8, 1992  15:46:16

METHOD NAME: M*CO2.MET

AREA%
      RT      AREA TYPE  WIDTH      AREA%
    6.722  5576330   UU   .341  22.79506
    7.673   301759   UU   .394   1.23354
    9.665 18584784 I UH  1.833  75.97139
```

Figure 7: Gas Chromatographic Trace Showing the Presence of Nitrogen (N_2) Formed as a Reaction Product During the Oxidation of Chloroacetonitrile in a He/O_2 Mixture.

Figure 8: Effluent Concentration (ppb) as a Function of Temperature for the Oxidation of 2-Chloroethyl Ethyl Sulfide Over the Automotive and MAP Catalysts. [C] = 50 ppm, τ = 0.03 s.
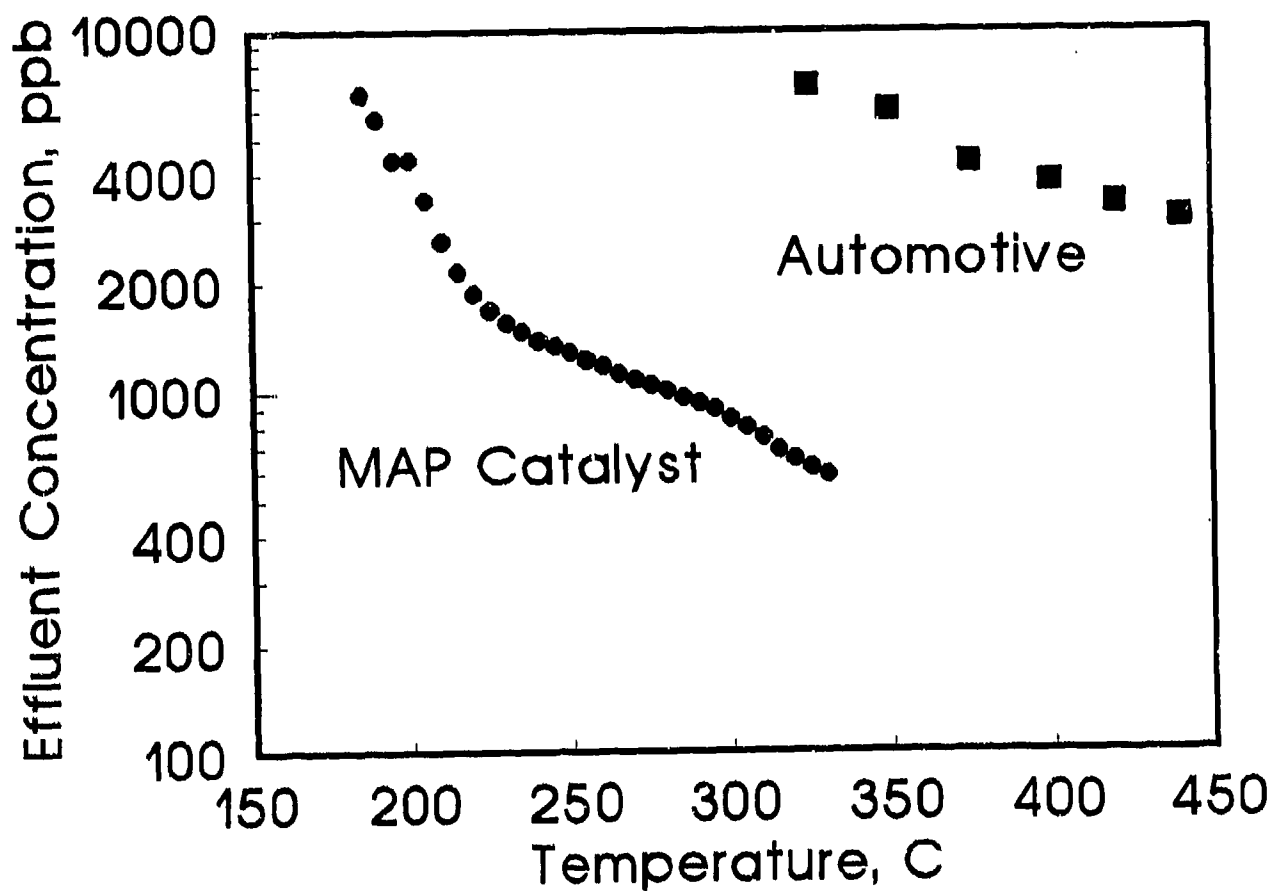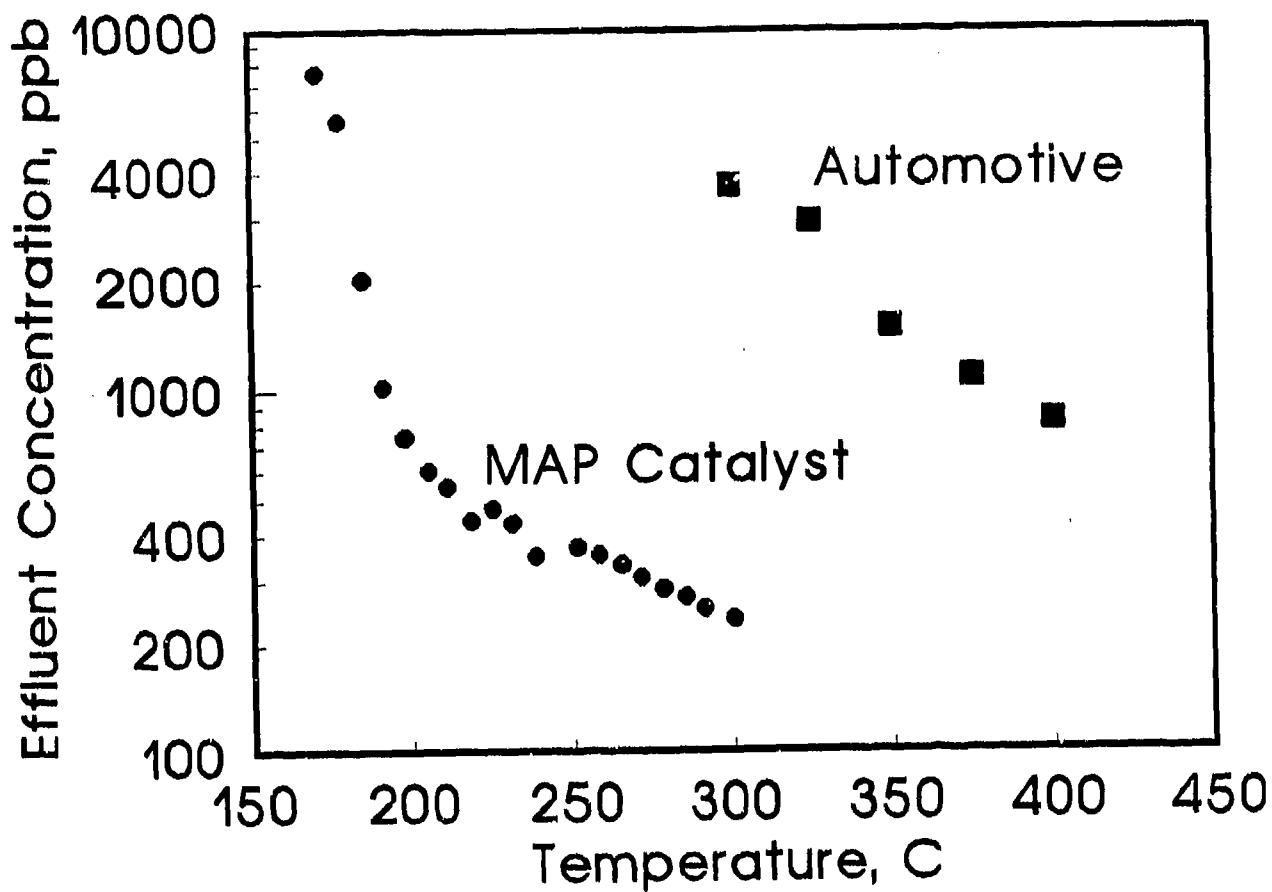
Figure 9: Effluent Concentration (ppb) as a Function of Temperature for the Oxidation of 2-Chloroethyl Ethyl Sulfide Over the Automotive and MAP Catalysts. [C] = 50 ppm, τ = 0.05 s.

temperature. The detection limits of 2-chloroethyl ethyl sulfide in the reactor effluent were approximately 40 to 50 ppb. The effluent concentration does not decrease at a significant rate for either catalyst as the reaction temperature is increased above about 220 °C. For both catalysts, the apparent activation energy (calculated at reaction temperatures greater than about 220°C) was approximately 1,700 cal/mol. This result indicates that external mass transfer resistances are severely limiting the observed reaction rate. The performance of the MAP catalyst in the mass transfer controlled regime is significantly greater than that of the Automotive catalyst. For example, at 300°C and a residence time of 0.05 seconds, employing the MAP catalyst results in decreasing the effluent concentration from 4,000 to 250 ppb. The improved mass transfer properties associated with the MAP catalyst may be attributed to a greater channel density.

4.   CONCLUSIONS

1) The reactivity and internal mass transfer properties associated with the washcoat of the MAP catalyst are superior to that of the Automotive catalyst.

2) The external mass transfer properties associated with the MAP catalyst are superior to those of the Automotive catalyst.

3) The oxidation of chloroacetonitrile over the MAP catalyst results in the formation of nitrogen gas (N_2) in near stoichiometric proportions.

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APPENDIX A: SAMPLE CALCULATIONS

Calculation of Apparent First Order Rate Constant:

The apparent first order rate constant was calculated as follows:

$$k = \frac{1}{\tau} \ln \frac{1}{1-x}$$

where k is the rate constant (s^{-1}), τ is the residence time (s), and x is the fractional conversion (dimensionless).